

IMPURITY REMOVAL IN THE BAYER PROCESS

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Presenter's Bio



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- **Present position: Director, Bauxite Residue R&D**
- **Work experience: Over 30 years in technical management and research roles in Bauxite/Alumina with companies such as Alcoa, Worsley Alumina and BHP.**



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- **How Impurities Affect Productivity**
- **Major Impurities and Removal Technologies**
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Introduction

- **Refineries are designed around the bauxite.**
- **Impurities can play a substantial role in design and operation**
- **Most impurities are managed through ‘natural’ sinks**
- **High relative inputs require dedicated removal processes**
- **Impurities that mostly affect product quality are not covered in this talk.**
- **Thousands of impurity removal concepts, very few in commercial use**



Some Typical Bauxite Ores

Species	Guinea	Brazil	Weipa	WA (1)	WA (2)	India	Jamaica
Al ₂ O ₃ Tot.	49.41	53.4	55.7	37.2	38	48.5	46.8
SiO ₂ Tot.	1.7	4.2	5.8	15.5	2.8	2.7	1.98
Fe ₂ O ₃ Tot.	19.06	13.9	11.9	24.5	35	17	19.2
CaO	0.01		0.01	0.01	0.01	0.02	1.13
C inorganic	0.06	0.01	0.03		0.1		0.4
C organic	0.11	0.03	0.23	0.2	0.2	0.11	0.2
S total	0.032	0.04	0.03	0.09	0.1	0.05	0.08
P ₂ O ₅	0.14	0.02	0.07	0.02	0.015	0.13	0.38
TiO ₂	2.94	1.1	2.7	2	2.7	5.32	2.25
MnO	0.02	0.01	0.03	0.006	0.003	0.04	0.32
V ₂ O ₅	0.05	0.04	0.06	0.06	0.05	0.19	0.11
ZnO	0	0	0	0.002	0.003	0.008	0.03
F				0.08	0.06		

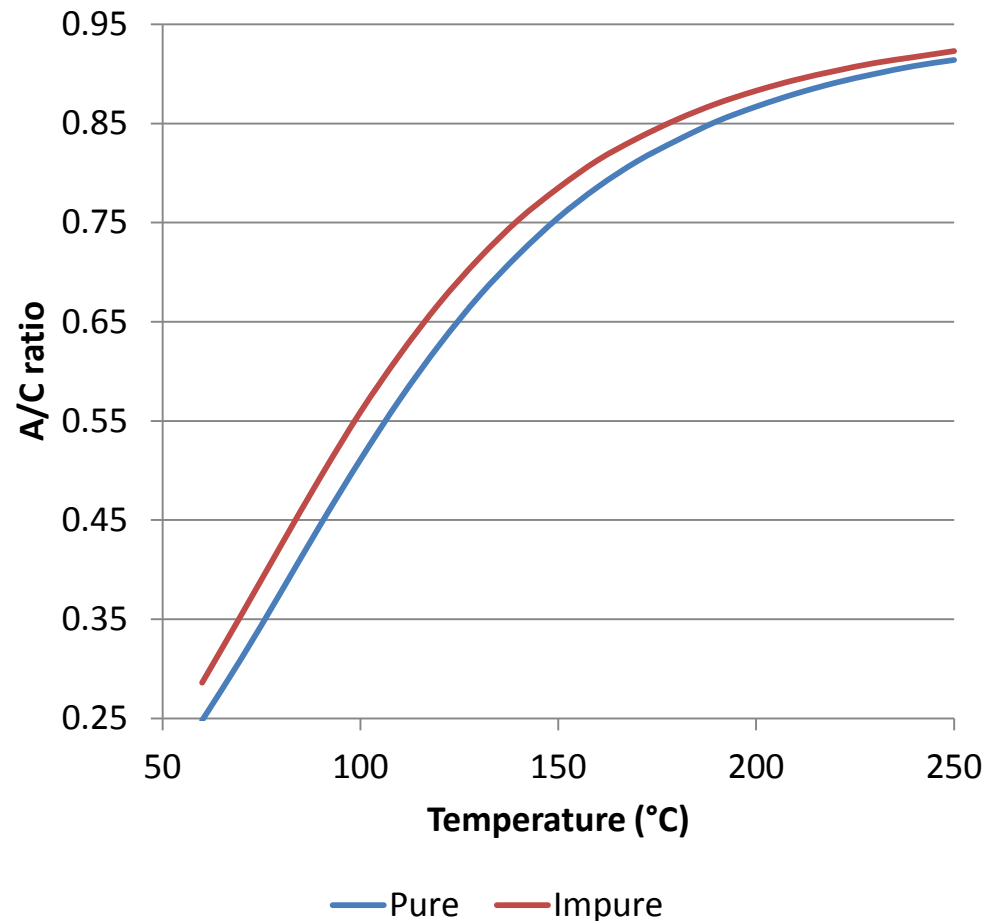


- **Wide range of impurities both inorganic and organic.**
- **Wide range of species extracted under Bayer conditions.**
- **Most impurities are controlled to ‘acceptable’ levels through DSP and soluble losses.**
- **Most refineries have effective control systems for carbonate and oxalate.**
 - Not always efficient.
- **Ideal solutions for TOC, sulphate and some other impurities yet to be found.**
- **Drive for Bauxite residue use puts pressure on purging for impurity control**



How Impurities Affect Productivity

- Increase in ionic strength alters OH^- and $\text{Al}(\text{OH})_4^-$ activities.
- Yield effects
- Product quality controls (e.g. oxalate).
- TS limits 'C'.
- Surface chemistry effects (e.g. rate).
- Scale (availability and op factor).

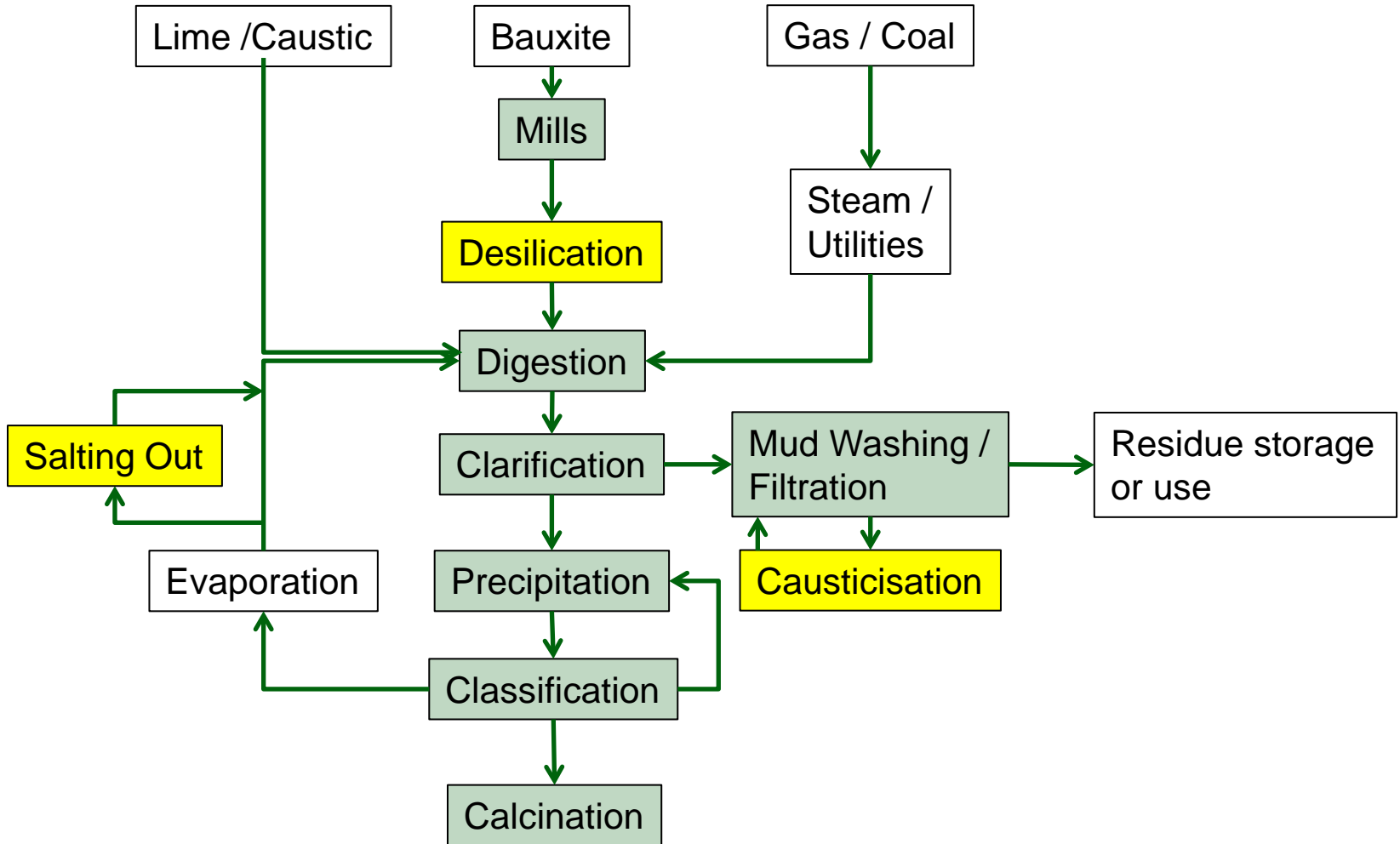


Carbonate

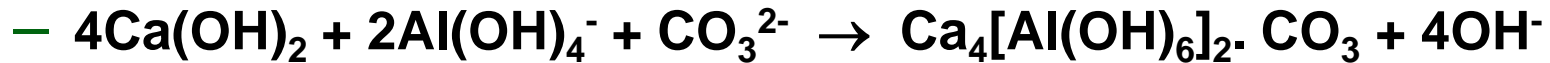
- **Relatively small inorganic input**
- **Most carbonate formed through base-catalysed cleavage of organics in digestion**
- **Some carbonate enters via lake water by CO₂ dissolution or photocatalytic breakdown of organics**
- **Removal via:**
 - **Intercalation in DSP**
 - **Causticisation**
 - **Salting-out**



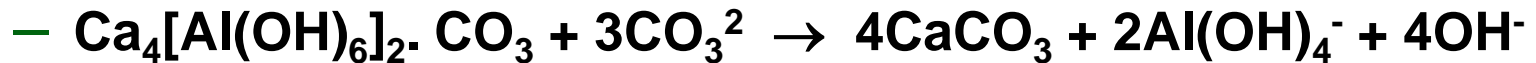
Carbonate Removal



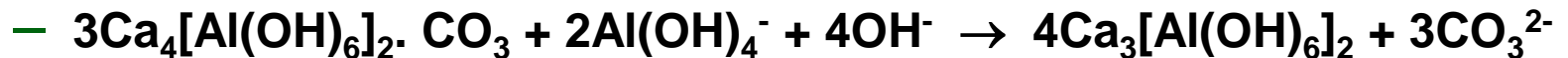
- **Causticisation reactions**



- (Hydrocalumite hemicarbonat or monocarbonat)

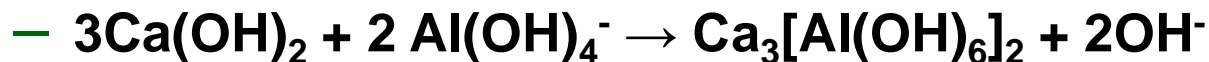
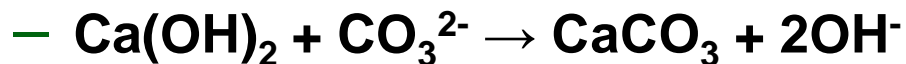


- Formation of calcium carbonate



- TCA formation

- **Overall Reactions**



- **Causticisation**

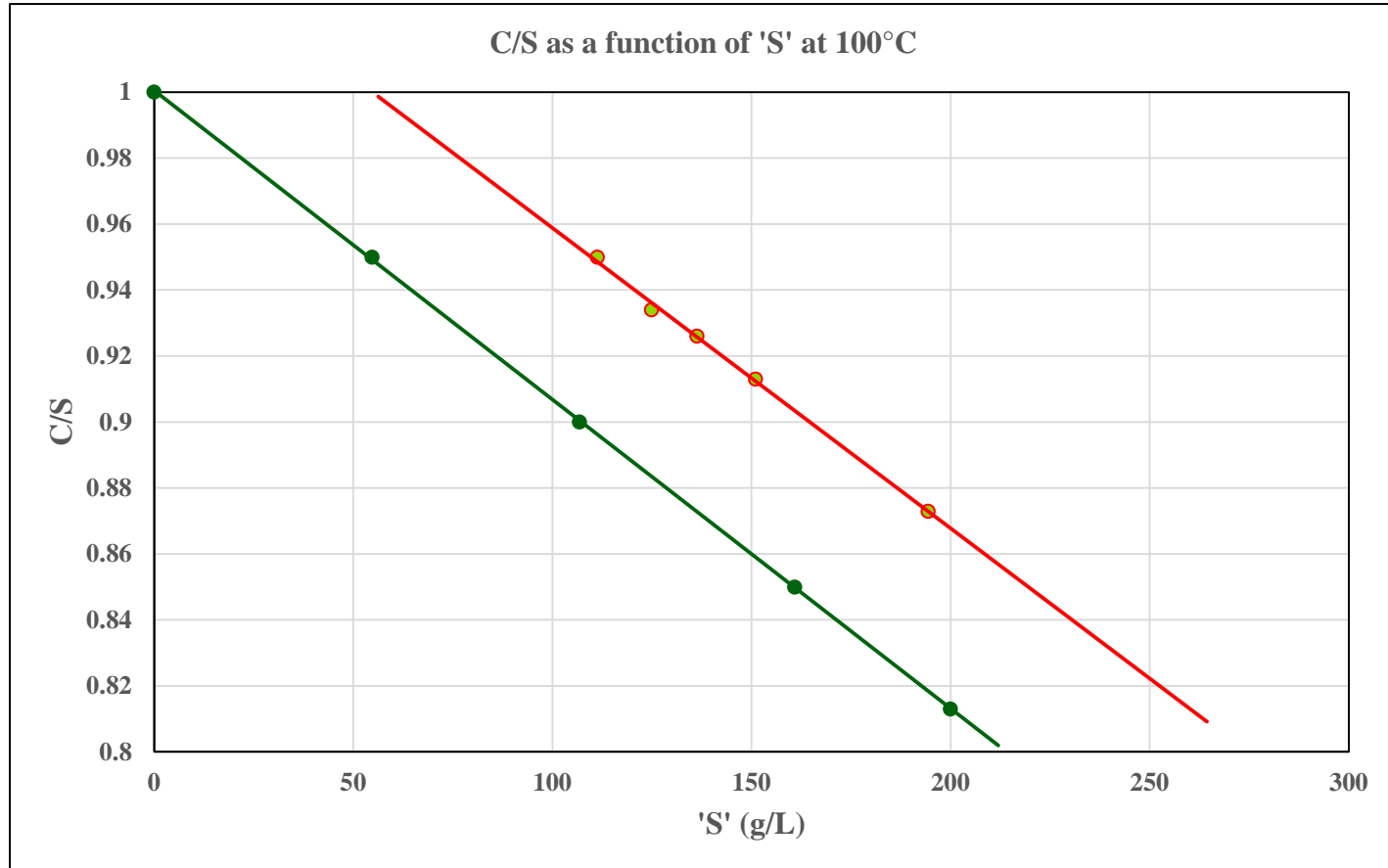
- Typical lime efficiency is about 50%
- Can increase this to over 90% by limiting TCA formation
 - Worsley TCA inhibitor
 - Worsley and Alcoa – High Temperature Causticisation (HTC)

- **Salting Out**

- Deep evaporation of spent liquor
- Product often includes other species including sulfate and oxalate
- HMW organics tend to produce a sticky cake that is difficult to handle
- Disposal an issue



Effect of TCA Inhibitor



Equilibrium C/S showing the effect of a TCA inhibitor

● without TCA inhibitor ● with TCA inhibitor



ICSOBA

Hamburg, 2 – 5 October 2017

Sulfate - Inputs

- **Mostly enters via sulfate/sulfide minerals**
 - Kaolin, jarosite, oxidation of pyrite or marcasite
- **Other sources:**
 - Gypsum
 - Sulfides added for Zinc control
 - Degradation of sulfur-containing organics
 - Cleaning acid



Sulfate – outputs

- **Major sinks are DSP and soluble losses**
 - Most sulfate removed via intercalation in sodalite (templates around sulfate anion)
 - Less so with cancrinite
 - Entrained liquor in residue



Sulfate – outputs

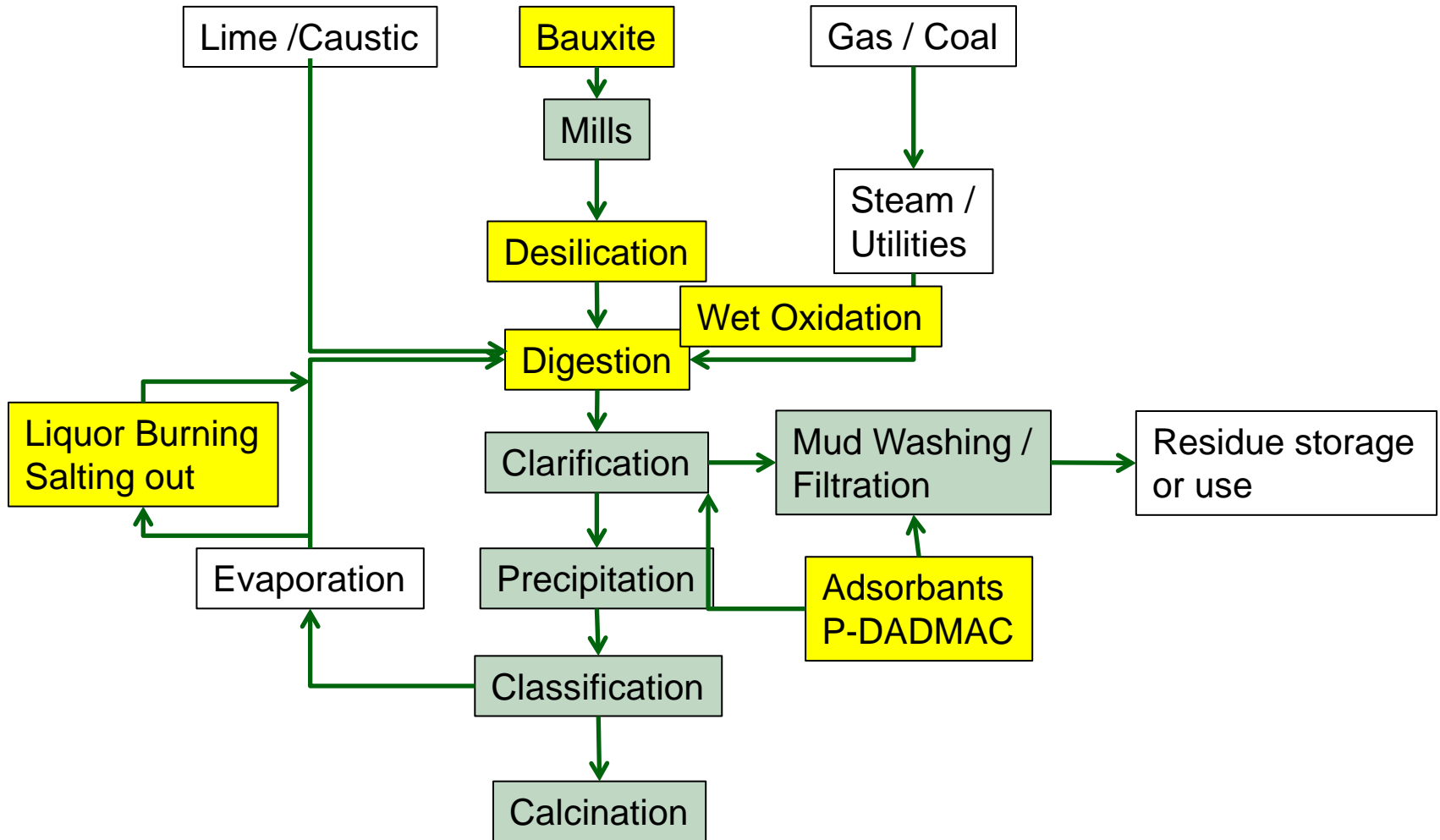
- **Other Removal Strategies:**
 - **Salting out ($\text{Na}_2\text{CO}_3 \cdot 2\text{Na}_2\text{SO}_4$, $\text{Na}_2\text{SO}_4 \cdot \text{NaF}$)**
 - Cake performance due to organics, disposal
 - **Salting out / liquor burning**
 - Filtration issues
 - **Cooling ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$)**
 - Energy, scale formation
 - **Layered double hydroxides (hydrocalumite, Lithium LDH)**
 - Cost, alumina loss



- **Vast range of organic species in bauxite**
 - Intact materials (plant and animal matter)
 - Cellulose, lignin, humic and fulvic acids (HMW)
 - Degraded matter (simpler organics)
- **HMW organics cause the most problems due to tendency to absorb on surfaces**
 - Surface chemistry impacts such as impurity incorporation, yield effects, morphology changes, and filtration problems
- **Base-catalysed hydrolysis results in simpler organics and ultimately carbonate, oxalate and other carboxylates**
- **Can contribute substantially to ionic strength**



Organics Removal



- **Adsorption**

- Inert, high surface area materials
 - Activated charcoal, magnesia, dolomite, hydrotalcite, TCA, alumina
- Problems: Separation, poor performance/cost, efficacy

- **Membranes**

- Polysulfone based ultra- and nano-filtration, cross flow systems
- Problems: poor permeate flux rates, fouling (including suspended solids), doesn't really *remove* organics, costly.

- **Anion Exchange (polyDADMAC)**

- Effective for some HMW organics, in relatively common use.
- Problems: Expensive, exchanges organics for chloride



- **Wet Oxidation**

- Effective for many organics (esp HMW), relatively economical to install/run.
- Problems: Hydrogen explosion risk, extreme conditions required for refractory organics, Separation, poor performance/cost, efficacy

- **Liquor Burning**

- Highly effective – removes all organics in treatment stream
- Problems: High capex/opex. Can be unreliable. Odours, halide emissions and caustic dust. Highly energy inefficient. Workforce/community issues.
- SLC a viable option, with few reported incidents.



- **Bauxite Roasting**

- Calcination of bauxite prior to digestion, producing transition aluminas and goethite-haematite conversion
- Problems – demonstrated at pilot scale, but never applied. Likely very high Capex/Opex, energy/GHG, odour and dust control issues.

- **Other techniques**

- Oxidative: MnO_2 , plasma torch
- Biological – Demonstrated for oxalate, could be extended to other carboxylates.
- Geopolymer – reaction of a side-stream of liquor with active silica to produce a geopolymer solid that supposedly entombs all impurities.

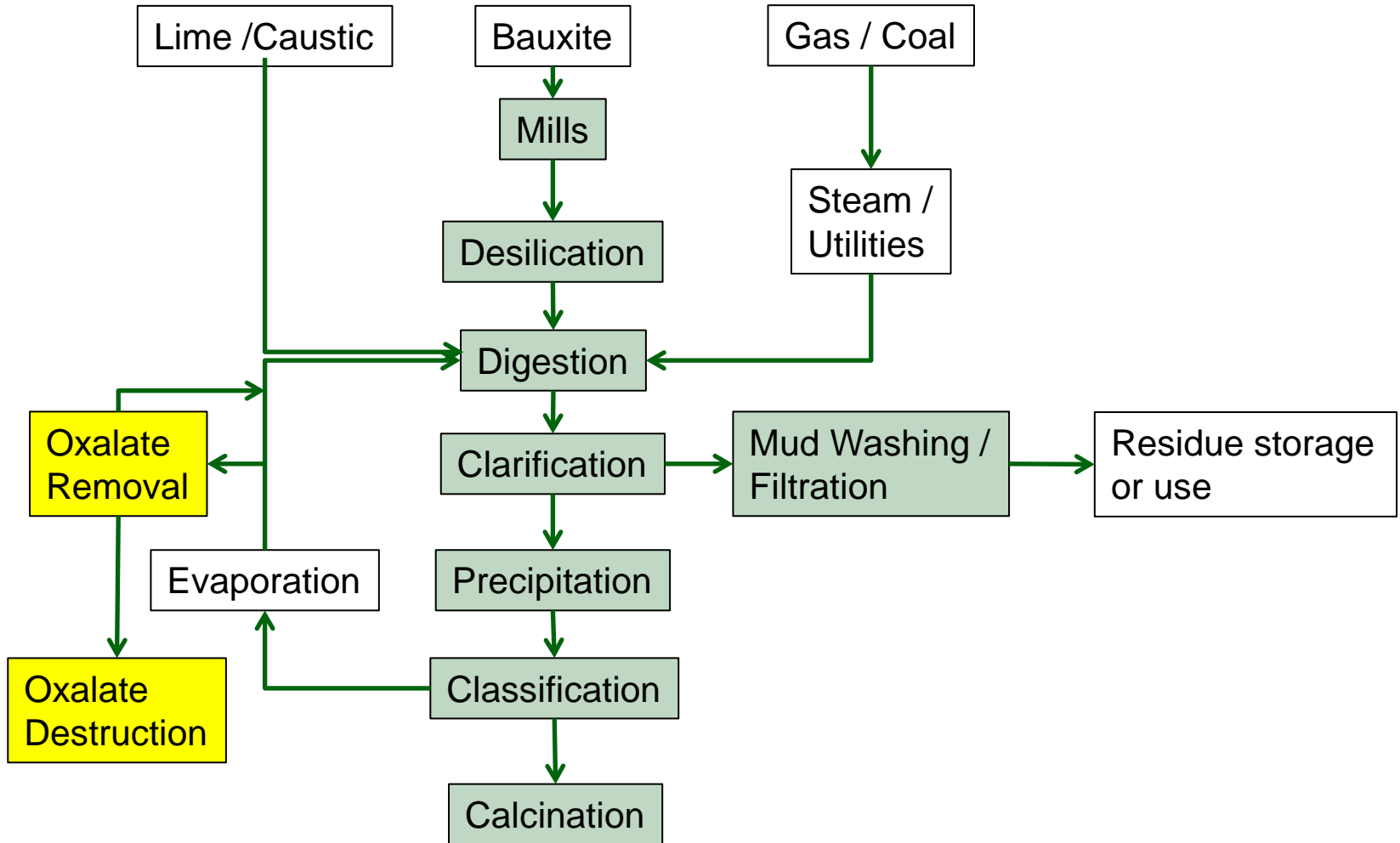


Oxalate - Inputs

- **Most oxalate produced through base-catalysed cleavage of more complex organics**
- **Small amount adsorbed on mineral surfaces**
- **Some oxalate present as oxalic acid (mainly in bauxite overburden)**



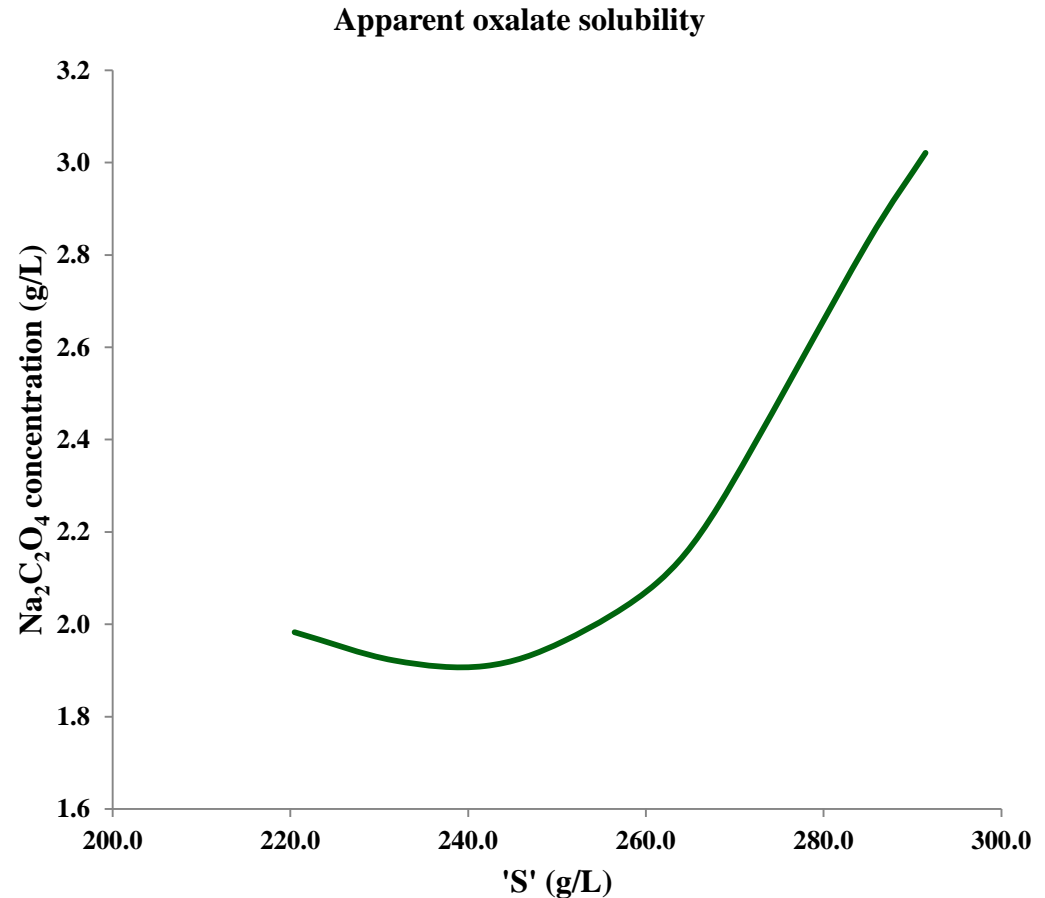
Side-stream Oxalate Removal



Oxalate – Side-stream removal

Evaporation/crystallisation

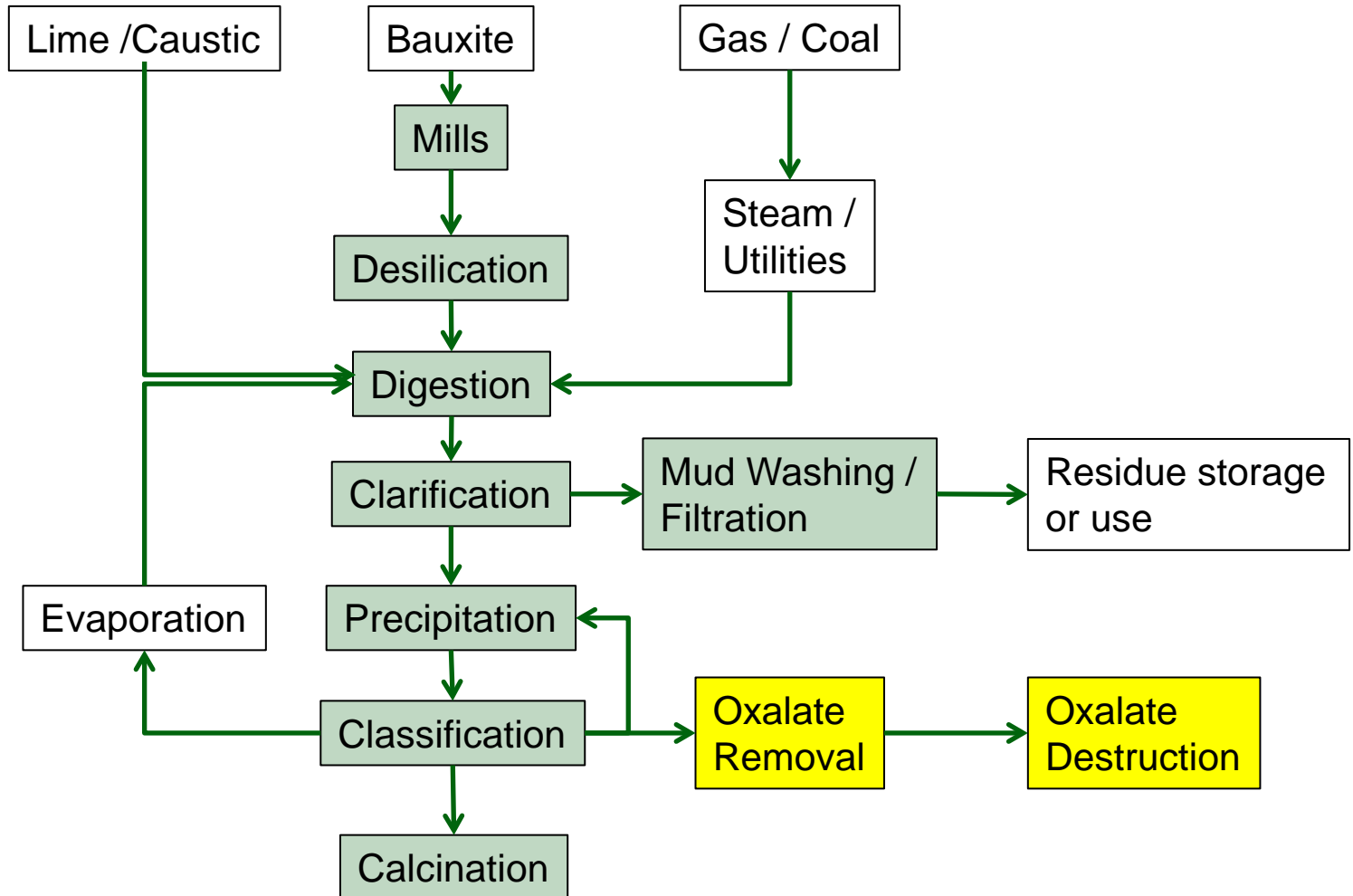
- Very common, reliable removal method. Moderate evaporation, with recycled oxalate seed. Crystals separated by filtration and discarded or destroyed,
- Problems: Oxalate morphology (filtration), yield can be poor, strongly affected by HMW organics and other surfactants. P-DADMAC can help.



- **Salting Out (deep evaporation)**
 - Commonly used, removes multiple impurities
 - Problems: poor oxalate morphology, often heavily contaminated with HMW organics. Very difficult to filter or settle.
- **“Drowning” out**
 - Alternative to Salting Out, decreases water activity by addition of partially miscible alcohols to supersaturate oxalate
 - Problems: Cost (solvent recovery), flammability, odours.
- **Sonocrystallisation**
 - Induces oxalate crystallisation by cavitation. Improved oxalate yield in pilot trials
 - Problems: Oxalate morphology, cake separation



Oxalate Co-precipitation



Oxalate Removal - Coprecipitation

- **Oxalate permitted to precipitate with gibbsite in precipitators**
- **Oxalate reports to fine seed and is washed out in counter-current washing tanks and filters.**
- **Fine seed must be (almost) oxalate-free to avoid severe product quality issues.**
- **Oxalate-rich washings must be treated to remove oxalate.**



- **Sodium oxalate is toxic and soluble.**
- **Roasting/calcination**
 - $\text{Na}_2\text{C}_2\text{O}_4 + \frac{1}{2}\text{O}_2 \rightarrow \text{Na}_2\text{CO}_3 + \text{CO}_2$
 - Carbonate can be returned to process and causticised
 - Problems: Odour, dust emissions
- **Causticisation**
 - Very common means of destruction. Oxalate from seed-washing or cake redissolved in water is treated with slaked lime.
 - $\text{Na}_2\text{C}_2\text{O}_4 + \text{Ca}(\text{OH})_2 + \text{H}_2\text{O} \rightarrow \text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O} + 2\text{NaOH}$
 - Problems: Very lime inefficient (2-10%), alumina loss
- **Two Stage Causticisation**
 - Improved lime efficiency (hydrocalumite used for carbonate csn)
 - Problems: High Capex/Opex



Oxalate Disposal and Destruction

- **Photocatalytic Oxidation**

- Seedwashing filtrate or cake dissolved in water.
- Problems: Catalyst required for acceptable rates, slow or ineffective in alkali (oxidation potential).

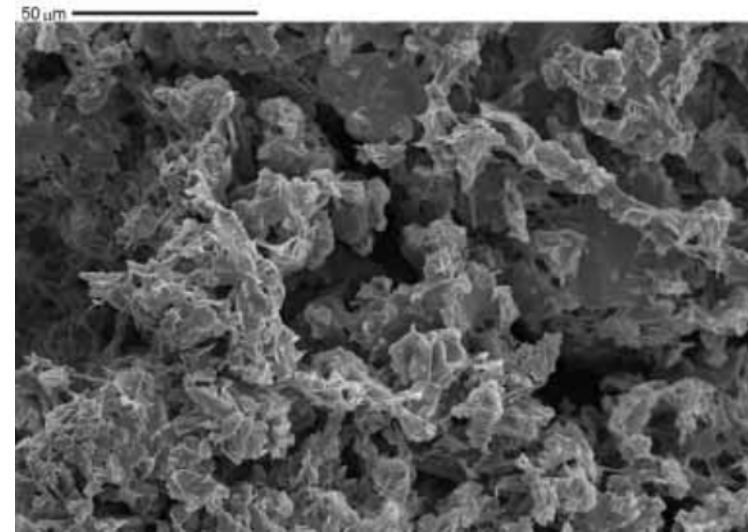
- **Biological destruction**

- Seedwashing filtrate or cake dissolved in water
- Extremophile oxalate consuming bacteria up to pH 11 in moving bed bioreactor.
- Very effective and simple to operate, produces sodium bicarbonate and sodium carbonate.



Fluoride

- Fluoride enters via clay, fluorspar etc.
- Typically removed with TCA
- Main issue is formation of sparingly soluble double salts that scale evaporators
 - $\text{Na}_2\text{SO}_4 \cdot \text{NaF}$ (kogarkoite),
 $\text{NaF} \cdot \text{Na}_2\text{V}_2\text{O}_5$ etc.
- With high sulfate, can also co-precipitate with gibbsite.
- At high concentrations, can remove by crystallising NaF.



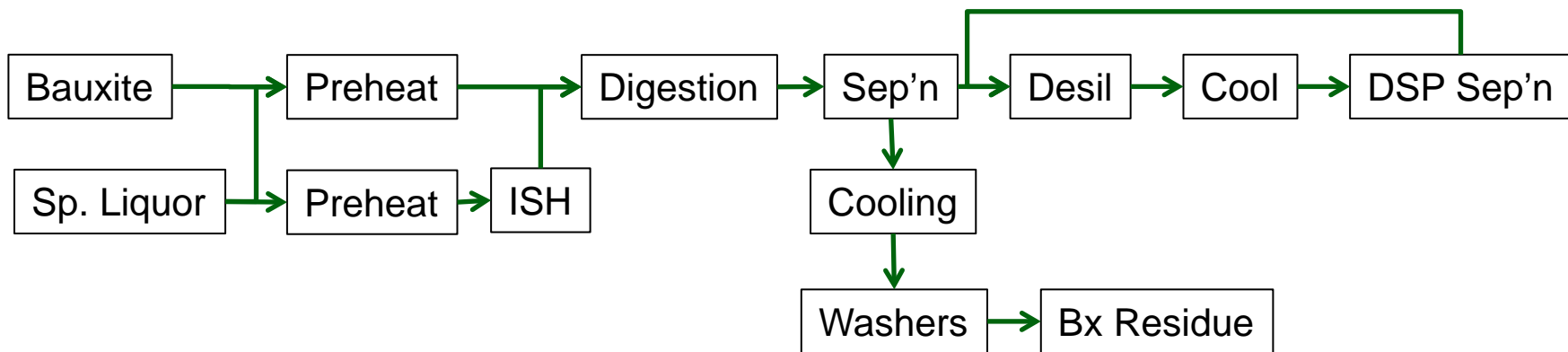
- **Very well known impurity – love/hate relationship!**
- **Pre-Desilication required for removal, with significant caustic loss**
- **Also main impurity removal process for many refineries (intercalation).**

- $3\text{Al}_2\text{Si}_2\text{O}_6(\text{OH})_4 + 18\text{NaOH} \rightarrow 6\text{Na}_2\text{SiO}_3 + 6\text{NaAl}(\text{OH})_4 + 3\text{H}_2\text{O}$
 - No net alumina loss unless quartz is attacked

- $6\text{Na}_2\text{SiO}_3 + 6\text{NaAl}(\text{OH})_4 + \text{Na}_2\text{X} \rightarrow \text{Na}_6[\text{Al}_6\text{Si}_6\text{O}_{24}]\cdot\text{Na}_2\text{X} + 12\text{NaOH} + 6\text{H}_2\text{O}$

- **Sumitomo process**

- Relies on relative dissolution rates of gibbsite vs kaolin
- Short digestion times, followed by rapid solid/liquid separation under pressure
- Liquor stream is separately desilicated, cooled and DSP filtered out. Possible soda and alumina recovery
- Problems: Loss of extraction efficiency, complexity, not suitable for boehmitic bauxites.



Bauxite Residue Impacts

- **Bauxite Residue (BxR) often considered the ‘sewer’ for the refinery**
- **For most BxR utilisation schemes, sodium is the main barrier**
- **High soluble losses or purging are incompatible with BxR use.**
- **Solid alkalinity (DSP, TCA, partially reacted lime solids) buffers pH and releases sodium**
- **Oxalate, sulphate and other impurities are also a problem.**



Conclusions

- **Thousands of impurity removal ideas have been proposed and tested, but relatively few have found commercial success.**
- **The reasons are mostly obvious: cost, operability and practicality.**
- **Impurity removal is an important part of refinery design**
- **Increasing pressure to make use of Bauxite residue demands that new ways to control impurities be found**

